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(54) Title: SOL-GEL PROCESS FOR THE PREPARATION OF VITREOUS FILMS POSSESSING HIGH ADHESION PROPERTIES AND STABLE COLLOIDAL SOLUTIONS SUITABLE FOR ITS CARRYING OUT THE SAME

(57) Abstract: Process for the preparation and the deposition of vitreous films on substrates comprising: the dissolution of one or more metal alkoxides in aprotic solvent, the hydrolysis of the resulting solution, the eventual removal of the formed alcohol, the deposition of the resulting sol on the substrate surface of interest and the final drying of the film.

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**Sol-gel process for the preparation of vitreous films
possessing high adhesion properties and stable colloidal
solutions suitable for its carrying out the same**

5 Description of the Industrial Invention having the title:
"SOL-GEL PROCESS FOR THE PREPARATION OF VITREOUS FILMS
POSSESSING HIGH ADHESION PROPERTIES AND STABLE COLLOIDAL
SOLUTIONS SUITABLE FOR CARRYING OUT THE SAME" in the name
of the Italian Company NOVARA TECHNOLOGY S.r.l. located in
10 Milano, viale E. Jenner, 51.

The present invention relates to a sol-gel process for the
preparation of vitreous films characterized by high
adhesion on the substrate of interest, to the vitreous
films obtained thereby,, and to the colloidal suspensions
15 obtained in the initial phase of the above mentioned
process, that can be removed and maintained as such for
indefinite amount of time, before being processed again to
achieve the film deposition.

More particularly, the object of the present invention is a
20 process for the preparation and the deposition, on the
surface of suitable substrates, of vitreous films
comprising the operations of dissolving one or more metal
alkoxides in an aprotic solvent, of adding controlled
amounts of an aqueous solutions of a catalyst to the
25 solution thereby obtained, of monitoring with adequate
precision the hydrolysis reaction, of the eventual
extraction and removal the amount of alcohol produced in
the hydrolysis reaction, of the gelation of the sol on the
surface of interest and of the final drying of the film. It
30 is of particular importance in this invention, the
possibility to stop the process after hydrolysis and before
film deposition to isolate a sol that in the apparent
condition of a clear and stable solution, can be stored
safely for long time at room temperature.

The vitreous films are used in the field of telecommunications on physical carriers for both optical and electronic applications; because of their remarkable resistance to temperature, abrasion and corrosion, silica
5 films are used, as an example, in processes typical of the electronic industry as surface planarizers in a semiconductor after previous treatments have created off-plane circuitry. Similar silica films are also used to produce electrical insulation between intracircuitry
10 elements or between conductors of different circuits on a semiconductor chip.

Moreover [A. S. Holmes et al., "Applied Optics", 1/9/1993, vol.32, n.25, pagg.4916-4912], silica films find applications as antireflexion and as planar wave-guides, or
15 even as host material for active dopants for nonlinear optic as well as optical sensing applications.

Many methods were developed for the preparation of optical devices [A. S. Holmes et al., ibidem], among other, as an example, can be called the thermic oxidation of silicon, or
20 the technique of deposition under reduced pressure, known as "sputtering", chemical vapor deposition, etc.

The technologies to which the above-cited methods refer are, however, relatively complex and sophisticated, their practical exploitation require specialized equipment and
25 time-consuming procedures that result in relatively costly operations.

Moreover, the limited productivity to which often they are coupled erodes the convenience for their industrial application.

30 It is a consolidated conclusion [A. S. Holmes et al., ibidem; Rui M. Almeida; "International Journal of Optoelectronics", 1994, vol.9, n.2, pagg.135-142], that the more promising technology for large scale production of

vitreous films is the sol-gel technology. Such a technology is based on three fundamental steps:

- a. sol formation in alcoholic medium (particle suspension or dispersion in a liquid),
- 5 b. gelation or transformation of sol by condensation into gel (a solid skeleton inglobating a continuous liquid phase),
- c. drying of the gel.

10 In the procedure for vitreous film deposition on substrate, the sol is applied to the surface to be coated and the gel is formed as consequence of the solvent evaporation; a drying phase by simple heating complete the coating procedure.

15 It is however known that in the production of vitreous films, even through sol-gel based technology one have to face limitations, specially in the thickness of the films obtained and/or in the tendency of such films to crack, often in the drying phase.

20 Solutions to the problem were promptly sought and some of technical answers reported in this field by the scientific literature and by recent patents, with no doubt contain preludes to future industrial application. Examples of such important reports are following:

25 - Italian patent application n. NO 98 A 00004 describes a sol-gel process for the preparation of thick films of silicon-dioxide that improves the well-known procedure by the addition of a certain quantity of fumed silica to the hydrolysis product of silicon alkoxide.

30 - A. S Holmes et al. already quoted article describes a process of high-temperature consolidation of a multilayers film.

- U.S. patent n.6.130.152 describes a sol-gel process that teaches to add a combination of two solvents with different boiling point to the hydrolyzed solution (tetraethylorthosilane, ethanol, water and acid).
- 5 - U.S. patent n.6.017.389 describes the preparation of siliceous films starting from the combination of tetraethylorthosilane and silica in anhydrous ethanol that is hydrolyzed by aqueous ammonia and necessitate of a very high thermal treatment at the end.
- 10 All the known solutions, of which the precedent paragraphs are only a few examples, make the sol-gel technology attractive for the preparation of vitreous films, but do not offer a fully convenient process for a broad industrial application either because of the temperature requirements
- 15 or because of thickness, or for particular technicalities that could negatively influence the industriability of the process.

The Applicant has now found that it is possible to prepare and to deposit on substrates, according to the sol-gel

20 technology, vitreous films following a procedure presenting none of the disadvantages of the known art, nor the limitations to general applicability so far reported on count of sol-gel technology.

As a matter of fact it is a first object of the present

25 invention a process for the preparation and the subsequent deposition on suitable substrates of vitreous films comprising the following steps:

- Preparation of a solution in an aprotic solvent of one or more alkoxides having the general formula

30
$$X_m - Me - (OR)_{n-m}$$

where Me is a metal belonging to groups 3°, 4° or 5° of the Periodic System of the Elements; n is the Me

valence; X is R_1 or OR_1 , with R_1 equal to or different from R, m is zero or an integer number equal to or lower than 3; R and R_1 are hydrocarbon radicals with a number of carbon atoms up to 12.

- 5 - Hydrolysis of the obtained solution in the presence of a catalyst by addition of water.
- Eventual removal of the alcohol formed during the hydrolysis reaction.
- Deposition of the sol on the substrate of interest.
- 10 - Final drying and stabilization of the film characterized by the fact that the preparation of the sol occurs in an aprotic medium.

The film deposition can be carried out immediately after completing the hydrolysis reaction, or the colloidal
15 dispersion obtained in this phase can be removed, whatever be the level of hydrolysis reached and stored indefinitely to be used at a desired time: this peculiar solution is characteristic of the process of the current invention and also define the second object of the invention as just here
20 stated: to provide a stable sol constituted by the hydrolysis products of an alkoxide corresponding to the above-reported formula, dissolved in an aprotic solvent, from which eventually the alcohol produced by the hydrolysis itself would have been removed. On this ground
25 are important aspects of the process of this invention the following:

- simplicity of preparation of the sol composition and stability thereof in time at room temperature;
- easiness of film casting, according to known techniques
30 executed under mild conditions and with acceptable times;

- rapid gelation times, with film remaining homogeneous and the mechanical characteristics of the substrate remaining unchanged;
 - not need for post-treatments.
- 5 As a consequence of such a process the films, also object of the present invention, are characterized by:
- high adhesion to substrate;
 - final shrinking without crackings;
 - good mechanical and insulating properties;
- 10 - good planarization capacity on the substrate surface;
- good optical properties.

Referring to the process for the preparation vitreous films according to the present invention, in the above alkoxide formula the "metal" can preferably be silicon and, among

15 all possible alkoxides, particularly suitable to the purposes of the present invention can be the following:

- tetramethylorthosilicate
 - tetraethylorthosilicate
 - tetrapropylorthosilicate
- 20 - tetrabutylorthosilicate
- ethyltriethoxysilane
 - methyltrimethoxysilane
 - methyltriethoxysilane

The alkoxide or mixture of alkoxides can be dissolved in a

25 suitable solvent and reacted with controlled amounts of water in the presence of a catalyst, preferably of acid or

basic character: the reaction can be accomplished, under agitation, at room temperature, for a time included between few minutes and few hours. The medium is an aprotic compound and can be preferably chosen among acetone,
5 tetrahydrofuran, dioxane; the alkoxide can be dissolved in such a solvent or mixture of solvent at a concentration between 30 and 60% by weight.

Hydrolysis reaction can be carried out through addition of controlled amounts of water, so to maintain the molar ratio
10 H_2O/Me between 0,5 and 5, preferably between 1,5 and 4 and, even more preferably between 2 and 3. As far as the acid catalyst is concerned, this might be any mineral or organic acid with K_a between 0,1 and 3.

The basic catalyst can be ammonia, other amines suitable
15 for the control of pH in the sol, or other suitable to the purpose

According to a preferred embodiment of the inventive process, the hydrolysis can be conducted in the presence of aqueous molar solution of HCl.

20 The molar ratio between alkoxide and acid can range from 1/0,001 to 1/1, but is preferably that such a ratio be maintained between 1/0,1 and 1/0,01. At the end of the hydrolysis reaction, the product has the appearance of a clear liquid, free from solid particles due to traces of
25 insoluble gels. It is possible at this point, according to an original and innovative aspect of the present invention, to obtain a sol with improved stability by elimination of the alcohol formed in the hydrolysis reaction.

The removal of the alcohol can be accomplished following
30 any methods known to the state of the art. To the purpose of exemplification the Applicant reports the experimental event that in the case of ethanol produced by the hydrolysis reaction, this is removed subjecting the sol to

a controlled partial desolventization in constant evaporation under reduced pressure, keeping the colloidal suspension at a temperature of about 40°C.

As previously mentioned, the process according to the present invention can be interrupted in its course after hydrolysis, thus obtaining a sol that is an object and an integral part of the present invention, characterized by high stability and such as to allow its long time storage without deterioration or contamination by insoluble precipitates that will compromise any further use thereof. The storage and conservation of such sol can simply be at room temperature.

The final sol so obtained after the hydrolysis reaction or after storage, is used for the deposition of the films having the characteristic properties already described. Deposition on the desired substrate does not present any particular difficulty and can be carried out according to the various techniques used in the known art as knife deposition, dip-coating, spin-coating. An important property of the sol according to the present invention is that of join to its high shelf stability its short time of gelation once deposited on the substrate. Referring, as an example, to the deposition for spin-coating the films are deposited in seconds using rotational speed of the order of 1500/2500 rpm and they do not any washing or post-treatments. The coated substrates can be moved immediately because the instant-gelation makes it solid at the time of removal from the spin-coater. In fact it is an important property of the film according to the invention to demonstrate excellent adhesion with regard to the majority of the substrates used in industry as, for example, silicon semiconductor wafers, gallium arsenide, polycrystalline silicon, glass, quartz glass etc..

The final drying of the film has the purpose to completely eliminate the residual solvent from the gel and to complete

the film stabilization; it can be conducted setting the film-substrates in an oven at temperatures between 80°C and 500°C. The operation is completed in 10-20 minutes time-span and is occurring without the appearing of

5 inhomogeneities and defects on the film due to impurities and or cracking caused by excessive shrinking of the gel in the drying phase.

According to an alternative embodiment of the inventive process, separate alkoxide solutions can also be prepared

10 the same undergoing hydrolysis at different times. The distinct sols obtained thereby can be used to deposit films on different samples of the substrate of interest on different substrates as well as on the same substrate according to a deposition order suggested by the skillness

15 or the technological needs, or they can be recombined into one sol of more integrated properties for better matching the specifications required in the deposited films.

Finally we should underline that in the process according to the present invention there are no problems concerning

20 film-thickness and it is possible to obtain any value of thickness, between 10 nm and 2 nm. The final thickness is controllable by monitoring concentration of network precursor into the sol as well alkoxide or alkoxide mixtures types entered. The Applicant has determined that

25 alkoxides corresponding to the above formula with X equal to R_1 contribute thickness higher than the ones of the film obtained via alkoxides where X is equal to OR_1 : special formulations of sol that controls film thickness through the use of different type of alkoxides is not only possible

30 but, at times very practical within the frame of the process of the present invention.

In the following are reported some achievements in the field of present invention only for the purpose of supplying practical examples without any limitation of the

35 invention itself to those embodiments.

Examples

Example 1:

Preparation of a sol based on tetraethylorthosilicate.

A 1l. round flask containing a magnetic stirrer bar is
5 loaded with 266g of an anhydrous acetone and 156,8g (0,75
moles) of tetraethylorthosilicate (TEOS). Keeping the flask
at room temperature, under constant stirring 32,4g of HCl
1M aqueous solution are added by slow dropping (molar ratio
TEOS: H₂O: HCl = 1: 2,3: 0,016). The addition of water
10 requires about 15 minutes. During this time the temperature
rises from 20°C to 40°C.

Stirring of the mixture is maintained for about 15 minutes,
then from what is now a clear liquid a volume of 50c is
collected and stored in a glass container with screw
15 stopper (Solution A).

With the same procedure an identical round flask is loaded
with 266g of anhydrous ethanol. The same procedure used to
prepare the acetone sol (solution A) is now used to prepare
an analogous sol in ethanol (solution B) both solutions are
20 left on the laboratory bench.

After 2 days solution B shows clear sign of gelation.
Solution A maintains its original status after 1 month
without any indication of gelation.

25 Example 2.

266g of anhydrous dioxane and 156,8g (0,75 moles) of
tetraethylorthosilicate (TEOS) are loaded on 1l. round
flask containing a magnetic stirrer bar. Following the
experimental procedures of example 1, 41,6g of 1M aqueous
30 HCl are added (molar ratios TEOS: H₂O: HCl = 01: 2,32:
0,016).

After 30 minutes a fraction of liquid (50ml) are removed from the flask and stored in a glass container with screw cap and called Solution C. The remaining solution is transferred to a rotating evaporator and subjected to
5 evaporation at a reduced pressure (about 100 tor) for about 20 minutes, keeping the internal temperature at 5°C and collecting about 80ml of evaporated liquid. The evaporation is interrupted and an equal volume of dioxane added to replace the ethanol solution removed. The evaporation is
10 restarted under the same conditions. In parallel, the concentration of ethanol in the evaporate is determined by gas chromatography. The operation of evaporation and replacement of evaporate with dioxane is repeated until the chromatographic analysis of the collected liquid shows 99%
15 extraction of ethanol generated in hydrolysis. A sample of 50ml of the sol so treated is transferred to a glass container with a screw cap and stored as Solution D. Solution C shows clear signs of gelation after 30 days, while Solution D maintains its original condition after 365
20 days without sign of gelation.

Example 3.

177g of anhydrous dioxane, 122g (0,588 moles) of TEOS and 68,4g (0,384moles) of methylthreethylorthosilicate (MTEOS)
25 are introduced in a 1l. round flask. Following the procedures of example 1, 41,6g of HCl 1M aqueous solution are added (molar ratios TEOS: MTEOS: H₂O :HCl = 1: 0,65: 2,22: 0,0416). After 30 minutes a fraction of 50ml of the liquid is removed, stored in a glass bottle with a screw
30 cup and labeled Solution E. The remaining liquid is set into a rotating evaporator and evaporated with the procedures of example 2 completing 3 cycles of evaporation and dioxane addition.

The chromatographic analysis of the evaporated solvents indicate that 99% of the ethanol produced in hydrolysis has been recovered. A sample of 50ml of the liquid remaining in the evaporator flask (sol) is removed, stored in a glass
5 bottle with a screw cap and labeled Solution F. Solution E shows clear signs of gelation after 30 days while solution F maintains its original condition without signs of gelation after 365 days.

Claims

1. A process for the preparation and the deposition of vitreous films on substrates comprising the following steps:
 - 5 - preparation of a solution in an aprotic solvent of one or more alcoxides corresponding to the formula
$$X_m - Me - (OR)_{n-m}$$
where Me is a metal belonging to groups 3°, 4° e 5° of the Periodic System of Elements; m is the valence of Me; X is R₁ or OR₁, with R₁ equal or different from R, m is either zero or integer number equal to or lower than 3; R and R₁ are hydrocarbon radicals with a number of carbon atoms equal to or lower than 12;
 - 10 - hydrolysis of the obtained solution in the presence of a catalyst;
 - 15 - eventual removal of the alcohol formed during the hydrolysis reaction;
 - deposition of the sol on the substrate of interest;
 - final drying and stabilizing of the film.
- 20 2. Stable colloidal solution obtained by hydrolysis, with eventual removal of the alcohol byproduct, of a solution in aprotic solvent of one or more alcoxides responding to the formula reported in claim 1.
- 25 3. Process for the preparation and deposition on substrates of vitreous films according to claim 1 in which the alkoxide is preferably selected among tetramethyl-ortosilane, tetraethylortosilicate, tetrapropylorthosilicate, tetrabutylorthosilicate, ethyltriethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, or mixture of the same.
- 30

4. Process for the preparation and deposition on substrates of vitreous films according to claim 1 where the aprotic solvent is preferably chosen between acetone, tetrahydrofuran and dioxane.
- 5 5. Process for the preparation and deposition on substrates of vitreous films according to claim 1 where the alkoxide solution or mixture of alkoxides in the aprotic solvent is between 30% and 60% by weight.
- 10 6. Process for the preparation and deposition on substrates of vitreous films according to claim 1 where the hydrolysis of the alkoxide is accomplished through addition of a controlled quantity of water.
- 15 7. Process for the preparation and deposition on substrates of vitreous films according to the above claim where water is added in such a quantity as to maintain the molar ratio H_2O/Me between 0,5 and 5.
- 20 8. Process for the preparation and deposition on substrates of vitreous films according to the above claim where the ratio H_2O/Me is preferably between 1,5 and 4.
9. Process for the preparation and deposition on substrates of vitreous films according to the above claim where the ratio H_2O/Me is preferably between 2 and 3.
- 25 10. Process for the preparation and deposition on substrates of vitreous films according to claim 1 where the hydrolysis of the alkoxide is accomplished in presence of an acid catalyst selected among mineral and organic acids with K_a between 0,1 and 3.
- 30 11. Process for the preparation and deposition on substrates of vitreous films according to the above

claim where the reaction of hydrolysis is preferably made in presence of an aqueous solution of HCl.

12. Process for the preparation and deposition on substrates of vitreous films according to claim 10
5 where the hydrolysis of the alkoxide is accomplished in presence of a quantity of acid such to have a molar ratio alkoxide/acid between 1/0,001 and 1/1.
13. Process for the preparation and deposition on substrates of vitreous films according to the above
10 claim where the molar ratio between alkoxide and acid is preferably between 1/0,1 and 1/0,01.
14. Process for the preparation and deposition on substrates of vitreous films according to claim 1 where
15 the hydrolysis reaction of the alkoxide solution in aprotic solvent is followed by the removal of the alcohol byproduct.
15. Process for the preparation and deposition on substrates of vitreous films according to the above
20 claim where the removal of the alcohol is preferably made by subjecting the sol to partial and controlled desolventization.
16. Stable colloidal solution according to claim 2 when obtained with the process according to one or more of the claims from 3 to 15.
- 25 17. Process for the preparation and deposition on substrates of vitreous films according to claim 1 where the deposition of the film on the substrate of interest is accomplished through a technique selected among knife coating, deep coating and spin-coating.
- 30 18. Process for the preparation and deposition on substrates of vitreous films according to the above

claim where the deposition is preferably accomplished by spin-coating.

19. Process for the preparation and deposition on substrates of vitreous films according to claim 1 where
5 the final drying is accomplished at a temperature between 20 and 500°C.
20. Vitreous films obtained and deposited with the process according to claim 1 characterized in that they have:
- high adhesion to the substrate;
 - 10 - final reduction in thickness without cracking;
 - good mechanical properties;
 - good planarizing properties;
 - good optical properties.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP 03/07275

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C1/00 C03B8/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category "	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 704 851 A (ESSILOR INT) 10 November 1994 (1994-11-10) page 5, line 24 - line 27; claims ---	1-20
X	US 5 496 402 A (HAGIWARA YOSHIO ET AL) 5 March 1996 (1996-03-05) column 4, line 55; claims ---	1-20
X	US 5 626 923 A (FITZGIBBONS JERRY M ET AL) 6 May 1997 (1997-05-06) column 4, line 11 - line 23; claims column 5, line 57 - line 67 --- -/--	1-20

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP 03/07275

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>I. ARTAKI ET AL: "Solvent effects on the condensation stage of the sol-gel process" JOURNAL OF NON-CRYSTALLINE SOLIDS., vol. 81, no. 3, 1986, pages 381-395, XP002255490 NORTH-HOLLAND PHYSICS PUBLISHING. AMSTERDAM., NL ISSN: 0022-3093 page 391 -page 392 -----</p>	1-20

INTERNATIONAL SEARCH REPORT

International application No
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